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Synthesis of Efficiently Green Luminescent CdSe/ZnS Nanocrystals Via Microfluidic Reaction

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Abstract Quantum dots with emission in the spectral region from 525 to 535 nm are of special interest for their application in green LEDs and white-light generation, where CdSe/ZnS core-shell structured nanocrystals (NCs) are among promising candidates. In this study, triple-ligand system (trioctylphosphine oxide–oleic acid–oleylamine) was designed to improve the stability of CdSe NCs during the early reaction stage. With the precisely controlled reaction temperature (285 °C) and residence time (10 s) by the recently introduced microfluidic reaction technology, green luminescent CdSe NCs ($\lambda = 522$ nm) exhibiting narrow FWHM of PL (30 nm) was reproducibly obtained. After that, CdSe/ZnS core-shell NCs were achieved with efficient luminescence in the pure green spectral region, which demonstrated high PL QY up to 70% and narrow PL FWHM as 30 nm. The strengthened mass and heat transfer in the microchannel allowed the formation of highly luminescent CdSe/ZnS NCs under low reaction temperature and short residence time ($T = 120$ °C, $t = 10$ s). The successful formation of ZnS layer was evidence of the substantial improvement of PL intensity, being further confirmed by XRD, HRTEM, and EDS study.

Introduction

Colloidal luminescent semiconductor nanocrystals (NCs), also known as quantum dots (QDs), have attracted considerable attention as potential candidates for LED and displays, photoluminescent and chemiluminescent biological labels, and so on [1]. QDs with emission in the spectral range from 525 to 535 nm are of special interest for the preparation of white-light and QDs-based green LEDs [2, 3]. To date, pure green luminescence has been realized by binary CdSe NCs and pseudobinary (AB_xC_{1-x}) semiconductor alloy NCs, such as $CdSe_xS_{1-x}$, $Zn_xCd_{1-x}Se$, etc. [2–6]. The synthesis of these pseudobinary NCs usually involves high temperature and multi-step reaction, and the control over their size, shape, and composition was far from ideal as compared with CdSe NCs. While bare CdSe NCs tend to be oxidized, the reduced photoluminescence (PL) quantum yield (QY) is generally observed during the post processing for special purposes. Overcoating bare QDs with a higher-band-gap material as a shell can result in the improved QY of PL. One possible configuration is that both the valence and the conduction band edges of the core material are located in the band gap of the shell material. This makes carriers be strongly confined to the core material, enhancing their probability of radiative recombination. Typical examples are CdSe/ZnS, CdSe/ZnSe, and CdSe/CdS [7–9], among which ZnS capped CdSe NCs exhibit low cytotoxicity and excellent stability [10, 11]. Using CdSe/ZnS core-shell NCs to achieve $\lambda = 525$ nm emission highly requires small CdSe cores (about 2.5 nm in diameter). Such small NCs with narrow size distribution and high QY of PL are difficult to be synthesized in batch reactions, which involve low reaction temperature (<200 °C) and extremely short reaction time (<10 s) [2(b)]. Nevertheless, the elongated nucleation period under low reaction temperature usually leads to polydisperse size for the products, while the realization of short reaction time is challenging due to the difficulties associated with quenching the reaction in a short period by batch methods [6(b)]. Moreover, it is difficult to overcoat such small NCs

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with higher-band-gap inorganic semiconductor, which is indispensable to realize their high quantum efficiency, good stability, as well as reduced cytotoxicity.

The enhanced transfer properties of mass and heat in a micro environment facilitate the chemical synthesis with improved efficiency and reproducibility. The superiority of microfluidic reaction with regard to precise synthetic-condition control, on-line sample characterization, as well as parallel operation has been demonstrated based on the study of CdSe, CdS, and so on [12].

In this study, a triple-ligand system (trioctylphosphine oxide–oleic acid–oleylamine) was designed to synthesize small sized CdSe NCs, and a capillary microreactor was set up to realize the controllable residence time. For the as-formed CdSe NCs, zinc diethyl dithiocarbamate was utilized as an environmental-benign ZnS source to synthesize CdSe/ZnS core-shell structures, and UV–Vis, PL, EDS, XRD, as well as HRTEM were utilized to characterize the formed NCs.

Experimental Section

Chemicals

Cadmium oxide (CdO, SCR, 99.9%), selenium (Se, SCR, 99.5%), trioctylphosphine (TOP, Fluka, 90%), trioctylphosphine oxide (TOPO, Fluka, 98%), 1-octadecene (ODE, Fisher, 90%), oleic acid (OA, SCR, 90%), oleylamine (OLA, Fluka, 70%,), zinc diethyl dithiocarbamate (ZDC, Shanghai Dunhuang Chemical Plant, 99%) analytic grade methanol, and chloroform (SCR) were used directly without further processing.

Apparatus

UV–vis absorption spectra were measured at room temperature with a Cary 100 UV–vis spectrometer (Varian). PL spectra were acquired at room temperature with a Cary Eclipse spectrofluorometer on colloidal solutions with an optical density of less than 0.2 at the excitation wavelength (430 nm). PL quantum efficiency measurements were performed as described in Ref. [13], utilizing Rhodamine 6 G as a reference. Powder XRD measurements were performed on a D/max2550 X-ray diffraction system (Rigaku). Samples for XRD measurements were prepared by dropping a colloidal suspension of NCs in chloroform on a standard single crystal Si wafer and evaporating the solvent. A JEM-2100F high resolution transmission electron microscope (HRTEM) was used to evaluate the microstructures of the prepared NCs, and the sample was prepared by dipping an amorphous carbon–copper grid in a dilute chloroform dispersed NC solution, then the sample was left to evaporate at room temperature. Energy-dispersive spectrum (EDS) was acquired usinga scanning electron microscope (JSM-6360LV, JEOL) equipped with EDX (FALCON, EDAX, America).

Synthesis of CdSe NCs

In a typical synthesis, a Se stock solution was prepared by dissolving 79 mg of Se powder in 2 mL TOP. The obtained solution was further diluted with 2 mL ODE. Meanwhile, a suspension of 12.85 mg CdO, 0.25 mL OA, 2 mL OLA, and 1.75 mL ODE washeated at 150 °C with stirring to prepare a clear yellow cadmium precursor solution. Before being drawn into the syringes, the two stock solutions were thoroughly degassed. Details for the experiments can be found elsewhere [14].

Synthesis of CdSe/ZnS NCs

CdSe NCs were utilized as formed. Single-molecular ZDC (0.5 mmol) dissolved in TOP (2 mL), and OLA (2 mL) was chosen as S and Zn sources. The set-up exhibited in Fig. 1 was applied for the synthesis. During the operation, equal-volume solutions of CdSe and ZnS precursors were delivered by a syringe pump under the same flow rate; after being mixed by a convective micromixer, two stock solutions were entered into a heated PTFE capillary for the overcoating process.

Results and Discussions

In a batch reaction, the long response time for temperature stabilization makes it challenging to realize large-scale production of QDs under very short reaction time. Here, microreaction demonstrates its priority with regard to the precise control of reaction time, just by changing the flow rate or the length of microchannel. The triple-ligand system enables the formation of high-quality CdSe NCs at 285 °C and under very short residence time from 5 to 30 s, as shown in Fig. 2. Several features were observed in the absorption spectra, which pointed to the narrow size distribution. The increased residence time led to wide size distribution of CdSe NCs, which was evidenced in the continuously increased full width at half maximum (FWHM) of PL (Fig. 2b). All the samples showed emission spectra in the green window (from 516 to 535 nm) with fairly narrow FWHM of PL (29–36 nm). The overcoating of CdSe NCs with ZnS usually results in small red shift of PL peak. To achieve CdSe/ZnS NCs with pure green luminescence, the residence time of 8 s was used to prepare CdSe NCs with PL peak at 522 nm.

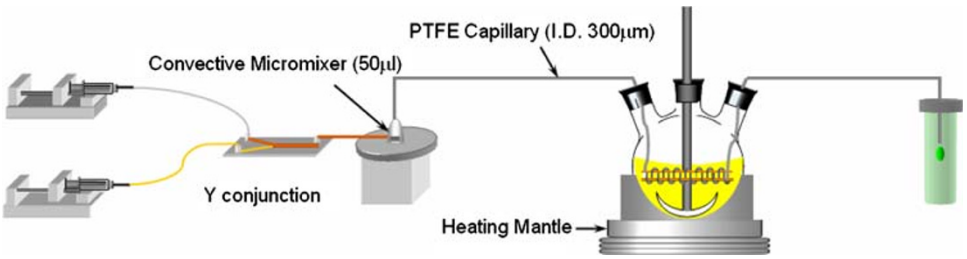

Fig. 1 Schematic graph for the set-up of capillary microreaction

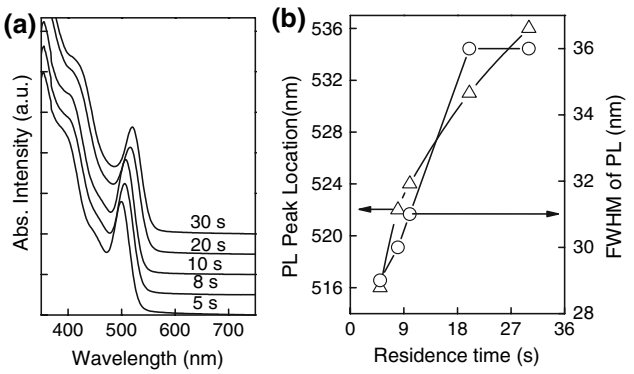

Fig. 2 (**a**) Absorption spectra and (**b**) PL peak location as well as FWHM of PL for CdSe NCs prepared at 285 °C under various residence times

Microfluidic reaction offers a convenient method to conduct chemical synthesis in a totally continuous fashion [15]. However, the continuous synthesis of CdSe/ZnS NCs via microreaction can be challenging, owing to the side reactions involved in the two-step reaction with multi-component precursors existing in the same solution. In this case, the temperature for the coating process shows significant importance: at higher temperatures, the CdSe cores begin to grow via Ostwald ripening, and deteriorate their size distribution, finally lead to broader spectral line widths; while the lower temperature will result in incomplete decomposition of the precursors and the reduced crystallinity of the ZnS shell.

Various temperatures and residence times were applied to optimize the overcoating process. After passing through the heated section, the previously yellow solution

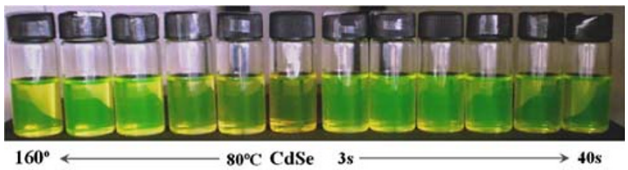

Fig. 3 Photographic demonstration for CdSe/ZnS NCs prepared with various temperatures and residence times under indoor light

demonstrated green luminescence even under indoor light, as shown in Fig. 3, indicating the improved PL QY of CdSe via overcoating. The successful formation of ZnS layer was evidently convinced by the red-shifted PL peak and improved PL intensity, because it was proved that the incorporation of either S or Zn into CdSe lattice would lead to green-shifted PL peaks. EDS analysis of the capped sample was made and is shown in Fig. 4a. The typical peaks for Se, S, Zn, and Cd were observed, among which S and Zn peaks were dominant. Figure 4b showed the XRD spectra of CdSe NCs and the overcoated counterpart prepared at 120 °C under the residence time of 10 s. Compared with the bare CdSe NCs, the diffraction peaks of the overcoated sample shifted to high angle, which is close to the pattern of wurtzite ZnS phase. This phenomenon further confirms the successful formation of ZnS shell around the surface of CdSe NCs.

Absorption and PL spectra for samples prepared under various temperatures waspresented in Fig. 5. With the increase of temperature from 80 to 160 °C, the PL peaks gradually red shifted to long wavelength, which could be due to the re-growing of CdSe NCs and partial leakage of the exciton into ZnS matrix [7]. To clarify the causes for

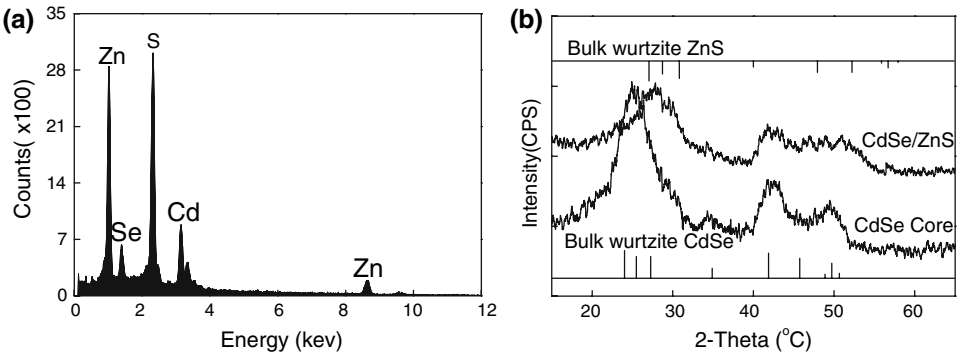

Fig. 4 (**a**) EDS spectra; (**b**) XRD spectra for CdSe/ZnS prepared at 120 °C with residence time as 10 s

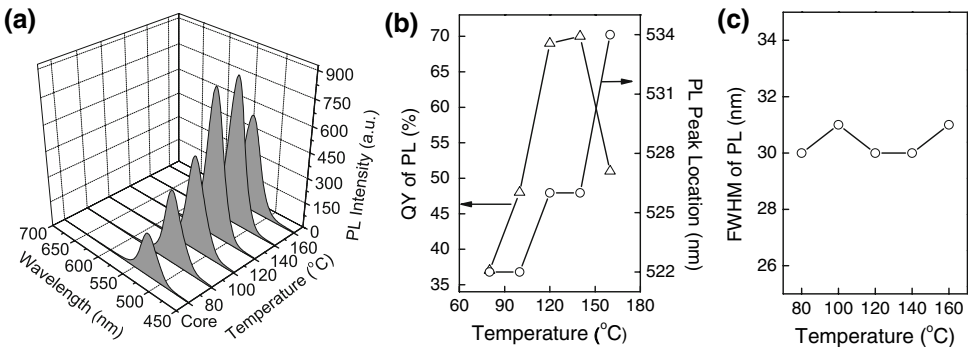

Fig. 5 (**a**) PL spectra; (**b**) and (**c**) PL peak location, PL intensity, and FWHM of PL for the CdSe/ZnS samples synthesized under changed temperature with the same residence time as 10 s

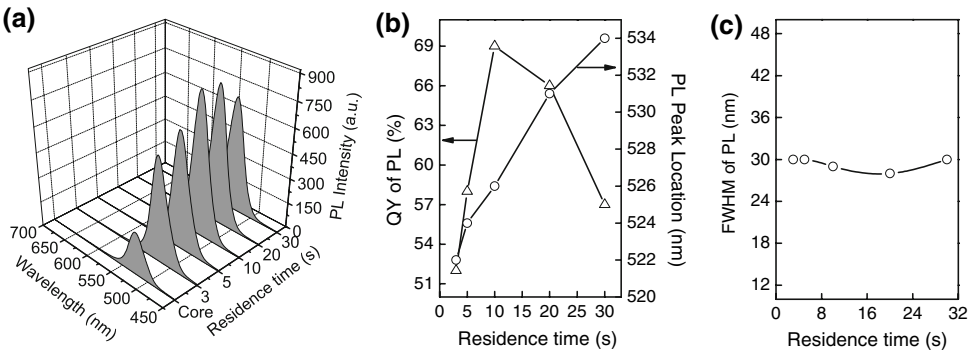

Fig. 6 (**a**) PL spectra; (**b**) and (**c**) FWHM of PL, PL peak location, and PL intensity for the CdSe/ZnS samples synthesized under various residence times at the same temperature as 120 °C

this red shift, the CdSe NC solution was passed through a heated capillary under the same temperature for the overcoating. No obvious change was observed from the absorption spectra, suggesting the low temperature used in the experiment was insufficient to trigger the growth of CdSe NCs. The "crossover" temperature for QY of PL was observed as 140 °C (Fig. 5b), which indicated the optimal ZnS thickness under this temperature. The encouraged decomposition of ZDC with the presence of OLA was provided as a justification for lowered temperature and shortened reaction time as compared with Wang's report [16]. For the overcoating temperature lower than 140 °C, the decomposition rate for $[(C_2H_5)_2NCSS]_2Zn$ was slow, resulting in the incomplete capping of daggling bonds on the surface of CdSe NCs. High temperature led to the improved decomposition rate of ZDC, resulting in the increased thickness of ZnS shell. Previous research regarding CdSe/ZnS NCs indicated that ZnS shell with the thickness of 1–2 monolayers resulted in the best QY of PL [7, 17]. For ZnS with thickness over 2 monolayers, the large mismatch (ca. 12%) between CdSe and ZnS lattice parameters can induce strain at the interface between the core and the shell, and the resulting defects in the ZnS shell throw negative effect on the PL efficiency. In this paper, the FWHM of PL was maintained at about 30 nm during the overcoating (as shown in Fig. 5c) confirming the homogenous coating of ZnS on the surface of CdSe. For temperature below 160 °C, the overcoating process exhibited excellent reproducibility, but the high temperature exceeding this threshold led to the evolution of gas due to the decomposition of ZDC.

Under the optimized temperature of 140 °C, high-quality CdSe/ZnS NCs could only be formed with fairly short residence time, and the elongated residence time over 10 s resulted in wide FWHM of PL. As a result, a lower temperature of120 °C was utilized to investigate the influence of residence time on the overcoating process. In this case, time resolved PL spectra were collected, and PL intensity, as well as FWHM of PL was utilized as an indirect index to

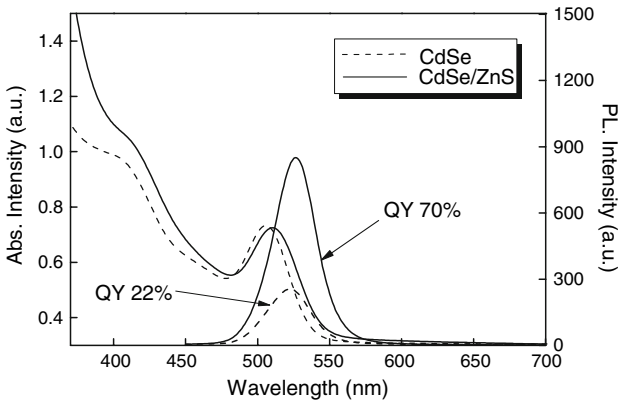

Fig. 7 Absorption and PL spectra for bare CdSe NCs and corresponding CdSe/ZnS NCs prepared at 120 °C for 10 s

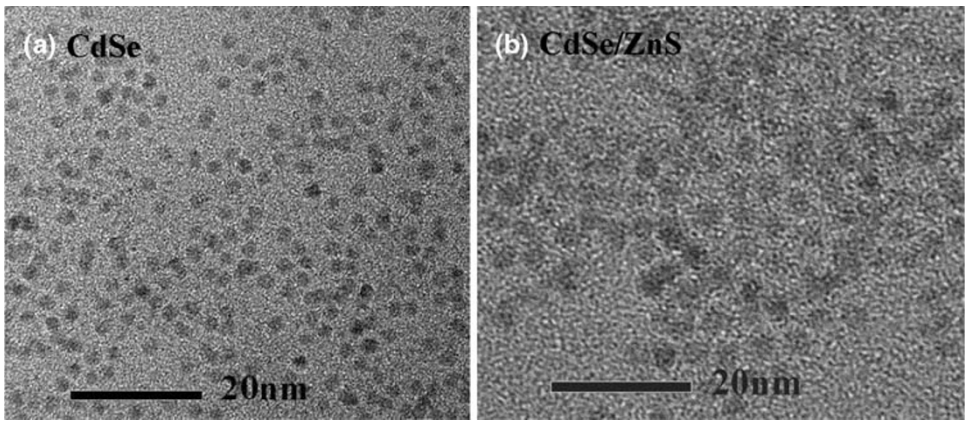

Fig. 8 TEM image for bare CdSe NCs and corresponding CdSe/ZnS NCs prepared at 120 °C for 10 s

evaluate the PL efficiency and size distribution. Most of the reports about the synthesis of QDs via microfluidic reaction seek to control the residence time by changing the flow rates [12], which will cause some instabilities on the final products, because the mixing efficiency and residence time distribution in a microchannel demonstrate strong relationship with flow rate. In this paper, residence time was controlled by changing the length of capillary in the heated section. With the increase of residence time from 3 to 30 s, a 12 nm shift of PL peak was observed, as shown in Fig. 6. Under a certain temperature, the elongated residence time results in the increased thickness of ZnS shell, and the accompanied leakage of the exciton into ZnS matrix led to red-shifted PL peak. The strengthened mass transfer in a microchannel facilitates the homogenous formation of ZnS shell, as confirmed by the maintained FWHM of PL for the samples prepared under different residence times (Fig. 6c). Significant improvement of PL intensity was even observed under the short residence time as 3 s, and four-fold increase of PL intensity over CdSe core was achieved for samples prepared under the residence time of 10 s (Fig. 6b). Here microfluidic reaction demonstrates its priority with regard to achieve best-quality products with the least reagent consumption and saved time.

With the optimized temperature and residence time, efficiently green luminescent CdSe/ZnS NCs (PL peak at 526 nm) can be reproducibly produced. The as-formed sample exhibited high QY of 70% at room temperature, as shown in Fig. 7. The overview TEM images (Fig. 8) clearly illustrated the narrow size distribution and fairly spherical morphology of CdSe NCs and CdSe/ZnS NCs with an average diameter of 2.4 and 3.6 nm, respectively. As a result, the best QY of PL was achieved for thickness of ZnS as two monolayers. The definition of a monolayer here is a shell of ZnS that measures 3.1 Å (the distance between consecutive planes along the [002] axis in bulk wurtzite ZnS) along the major axis of the nanoparticles [7].

Conclusions

In conclusion, a facile method was developed to prepare small sized CdSe NCs, and an environmental-benign precursor for S and Zn was utilized to synthesize core-shell structured CdSe/ZnS NCs with pure green luminescence. With the strengthened mass and heat transfer in the microchannel, highly luminescent CdSe/ZnS NCs were obtained under short residence time and low reaction temperature ($t = 10$ s, $T = 120$ °C). Homogenous coating of ZnS was achieved with fairly wide operation parameters. With the presented low temperature overcoating process, the purification process of CdSe NCs can be eliminated, which offered the feasibility to synthesize CdSe/ZnS NCs in a totally continuous fashion.

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